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Material behaviour

# Different aspects of the accelerated oxidation of polypropylene at increased pressure in an autoclave with regard to temperature, pretreatment and exposure media

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ABSTRACT

The aim of this study is to investigate and compare three different factors, temperature, pretreatment and exposure media, on the oxidation and aging behavior of polypropylene (PP) bulk samples in the autoclave test under increased oxygen pressure. The aging of polypropylene, in this case syringe material, was accelerated under different conditions. The samples were aged at 75°, 80° and 85 °C under pure oxygen and at 75 °C under ultrapure water. Further samples treated with 15 kGy (e-beam) were aged at 75 °C under pure oxygen. All experiments were carried out at an oxygen partial pressure of 50 bar. The different courses of aging were evaluated and compared. Color and transparency were used to assess the visual changes; weight, geometry and tensile test for the changes in technical properties; and DSC, FTIR and TDS-GC-MS to improve our physico-chemical understanding of the aging processes.

The investigations showed that all factors tested influence oxidation/aging behaviour. Dry or wet exposure has no effect on aging during the induction time. However, after the point of maximum service time the degradation process of polymer changes significantly in the presence of water. The increase of aging temperature decreases the maximum service time; however a temperature higher than 80 °C changes the relative ratio of surface and bulk oxidation. The pretreatment with irradiation decreases the maximum service time further, because the irradiation partly damages the antioxidant, and the mobility of antioxidant fragments inside the polymer changes. These diffusion effects influence the relative ratio of bulk and surface oxidation of the polymer sample.



## 1. Introduction

For research on geotextiles and geotextile related products, the autoclave test is well established to determine resistance of polyolefinic materials to oxidation. This accelerated aging process applies increased temperatures and oxygen partial pressure. Aqueous solutions must always be used as exposure media in these studies [1,2]. A great advantage of this method is the comparatively fast aging of polyolefinic materials, which have to be resistant for as long as several decades [3–8]. Although the life time prediction of such polymers is of high economic interest, the molecular understanding of the oxidation process during this test scenario is still insufficient.

Scientific works about accelerated aging with an autoclave can be found in the literature by E. Richaud et al. [6–8] and A. Astruc et al. [5]. They carried out their investigations on PP fibers (diameter ≈ 30 μm) at 80 °C, different pressures (2, 5, 10, 15 and 50 bar) and different exposure media (pure oxygen, neutral aqueous medium and alkaline aqueous medium). From their studies, they

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developed kinetic models in which the influences of different parameters (pressure, temperature, and stabilizers) were considered. They found that oxygen pressure and higher temperatures significantly increase the oxidation of PP; the higher the pressure the faster the oxidation. With higher pressure, the efficiency of stabilizers also decreases by direct attack oxidation of antioxidants.

In contrast to these works, our work deals with the oxidation process on real, bulk samples, the influence of different temperatures (75°, 80° and 85 °C) at 50 bar oxygen partial pressure and the influence of aqueous exposure media (pure oxygen and ultrapure water). In future work we will also consider lower oxygen partial pressures and the detailed role of the antioxidant for such bulk samples.

In order to better understand the process of oxidation and the aging behavior of PP, the samples were furthermore exposed to an e-beam dose of 15 kGy. E-beam is a common sterilization method for polymer products (e.g. in medical or food technology) [9]. It is known that irradiation has significant effects on the material, for example on antioxidants and chain scission [10–14]. Even small doses destroy antioxidants, and thus influence the oxidation and aging behavior of the material. This effect on the antioxidants is known from literature [13,14] and has been confirmed by our own Oxidation Induction Time (OIT) measurements.

For our investigations, syringes made of PP were chosen. In medical applications, only a limited number of possible additives are in use. Hence, the composition of the investigated material has been well defined over a long period of production and use [15].

In the work, the different courses of aging were evaluated and compared. Visual changes could be observed through changes in the material color and transparency. Technical characteristics were analyzed by observing changes in weight and geometry. Changes in tensile strength were also determined. To improve our physicochemical understanding, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and gas chromatography/mass spectrometry (TDS-GC-MS) were used. For a better overview, the results were divided into three categories: accelerated aging as a function of temperature, exposure media and pretreatment.

## 2. Experimental

### 2.1. Material

The materials used are syringe barrels made of PP. Both electron irradiated and non-irradiated samples were subjected to accelerated ageing in an autoclave. The average wall thickness of the barrels is 1 mm. They contain the antioxidants Irganox 1010 (~ 0.04 wt %) and Irgafos 168 (~0.04 wt %). The 15 kGy samples were irradiated by 10 MeV electron beam according to a standard procedure.

### 2.2. Accelerated aging with autoclave

BAM's own autoclaves a capacity of 7 l were used for the investigations. Temperature and pressure can be set as needed; the pressure range is $p_R$-95 bar and the temperature range $T_R$-95 °C. Aqueous solutions, nitrogen and oxygen are the possible exposure media. More details are presented in the literature [3,16].

Up to now, ultrapure water with oxygen partial pressure of 50 bar or pure oxygen with oxygen partial pressure of 50 bar have been used as exposure media. In each experiment, 39 barrels were stored in a designated holding device made of steel (19V4A). The irradiated material (15 kGy) was tested under pure oxygen at 75 °C, the untreated samples at three different temperatures (75°, 80° and 85 °C) under pure oxygen and at 75 °C under ultrapure water. In all tests, samples were taken after 24 h of exposure. The results measured after this day were set as base values to disregard the effects of adjusting to the physical aging conditions, such as post crystallization. The samples were taken after different intervals under the respective exposure conditions (Table 1). For each sampling day, two to three barrels were taken. The experiments were stopped as soon as the samples became too brittle for tensile tests or when the samples were completely consumed (only ultrapure water exposure). Before the beginning of the sample analysis, the samples were exposed to the standardized climate (23 °C, 50% relative humidity) for 24 h.

For safety, the change in the autoignition temperature ($T_{ig}$) of the material under pure oxygen at 75 °C exposure was controlled [2,17]. The outcomes are summarized in Table 2. In the first part of the table the $T_{ig}$ of the untreated samples is shown after different exposure times (0, 21 and 42 d); the second part shows the values for the sterilized samples (0 and 21 d). In both, the untreated and the sterilized material, the $T_{ig}$ falls after exposure. Of the material not stored, the sterilized sample has a $T_{ig}$ 10 °C lower than the untreated samples. The untreated material owns its $T_{ig}$ drop by about 20 °C after 42 d of exposure, and the sterilized material after 21 d. However, it remains far from the exposure temperature.

### 2.3. Weight and geometry measurements

Before exposure and one day after removal, the geometry and weight of each sample were recorded. For geometry data, the length, inner and outer diameters were measured with a commercially available digital caliper from Mitutoyo. The weight was determined using a Sartorius Analytic A200S digital balance with a standard deviation of ±0.0001 g. For each exposure day, at least two samples were measured and compared to their initial values. Figures display the mean values of the measurements. The standard deviation is less than 0.02%.

### 2.4. Tensile tests

Test samples 2 mm in width were punched from the syringe body. Tensile tests were realized using the universal Zwick 1445 class 1 testing machine (Zwick Ulm, Germany) with electronic force and displacement measurements and a constant rate in accordance with ISO 527. The tests were carried out at room temperature and the data obtained represents the average value of 10 test specimens. The standard deviation usually did not exceed 10%. There were only two exceptions: each of the last days of pure oxygen exposure at 75° and 85 °C, for which the standard deviation